

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

Mo6934/LeA 33.548

U.S. APPLICATION NO. (if known, see 35 CFR 1.5)

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To be Assigned

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/07260

28 July 2000 (28.07.00)

10 August 1999 (10.08.99)

TITLE OF INVENTION

Method for the Production of Three-Dimensional or Flat Structures

APPLICANT(S) FOR DO/EO/US KOPP, Richard, MAYER, Eduard, WOLFRUM, Christian

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Abstract page

PATENT APPLICATION
Mo-6934
LeA 33,548

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
RICHARD KOPP ET AL) PCT/EP00/07260.
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: METHOD FOR THE PRODUCTION)
OF THREE-DIMENSIONAL OR FLAT)
STRUCTURES)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231
Sir:

Prior to the examination of the subject application, kindly amend the application as follows:

"Express Mail" mailing label number ET671450083US
Date of Deposit February 5, 2002
I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231
Donna J. Veatch
(Name of person mailing paper or fee)
Donna J. Veatch
Signature of person mailing paper or fee

IN THE SPECIFICATION:

At page 1, and on page 17 (Abstract) delete the title and insert --METHOD FOR THE PRODUCTION OF THREE-DIMENSIONAL OR FLAT STRUCTURES --.

A new Abstract page is included herewith.

At page 1, line 2 insert the heading --BACKGROUND OF THE INVENTION--.

At page 2, line 4 insert the heading --SUMMARY OF THE INVENTION--.

At page 2, line 10 insert the heading --DETAILED DESCRIPTION OF THE INVENTION--.

IN THE CLAIMS:

Cancel Claims 1-9.

Kindly add the following claims:

- 10. A process for the production of three-dimensional or flat structures comprising combining and reacting at least two component jets wherein each component jet is in the form of small droplets with an average diameter of $<1000\text{ }\mu\text{m}$, and one component jet comprises a) at least one polyisocyanate component and another component jet comprises b) at least one component capable of forming polymers by reaction with a polyisocyanate component.
11. The process of claim 10 wherein the at least two component jets are combined droplet-by-droplet.
12. The process of claim 10 wherein at least one further jet is combined comprising at least one additive.
13. The process of claim 10 wherein at least one additive is added to at least one of the components of the jets a) and/or b).
14. The process of claim 10 wherein the three-dimensional or flat-structure is built up on a support element on reaction of the colliding jets.

15. The process of claim 10 wherein the jets of the components are combined above the support element.
16. The process of claim 15 wherein the jets of the components are combined on the support element.
17. The process of claim 10 wherein component b) comprises a polyamine.
18. The process of claim 10 wherein the production takes place in an atmosphere with a relative humidity of <40%.

REMARKS

Claims 1-9 have been cancelled and replaced by Claims 10-18. These claims are supported by the original claims. A new Abstract is enclosed.

An early action of the merits is respectfully requested.

Respectfully submitted,

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION:

At page 1, and on page 17 (Abstract) delete the title and insert --METHOD FOR THE PRODUCTION OF THREE-DIMENSIONAL OR FLAT STRUCTURES --.

A new Abstract page is included herewith.

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At page 2, line 4 insert the heading --SUMMARY OF THE INVENTION--.

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IN THE CLAIMS:

Cancel Claims 1-9.

Kindly add the following claims:

- 10. A process for the production of three-dimensional or flat structures comprising combining and reacting at least two component jets wherein each component jet is in the form of small droplets with an average diameter of $<1000\text{ }\mu\text{m}$, and one component jet comprises a) at least one polyisocyanate component and another component jet comprises b) at least one component capable of forming polymers by reaction with a polyisocyanate component.
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13. The process of claim 10 wherein at least one additive is added to at least one of the components of the jets a) and/or b).
14. The process of claim 10 wherein the three-dimensional or flatstructure is built up on a support element on reaction of the colliding jets.

15. The process of claim 10 wherein the jets of the components are combined above the support element.
16. The process of claim 15 wherein the jets of the components are combined on the support element.
17. The process of claim 10 wherein component b) comprises a polyamine.
18. The process of claim 10 wherein the production takes place in an atmosphere with a relative humidity of <40%.

METHOD FOR THE PRODUCTION OF THREE-DIMENSIONAL
OR FLAT STRUCTURESABSTRACT OF THE DISCLOSURE

The invention relates to a process for the production of three-dimensional or flat structures comprising combining and reacting at least two component jets wherein each component jet is in the form of small droplets with an average diameter of $<1000\text{ }\mu\text{m}$, and one component jet comprises a) at least one polyisocyanate component and another component jet comprises b) at least one component capable of forming polymers by reaction with this polyisocyanate component.

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Process for the production of three-dimensional or flat structures

This invention relates to a process for the production of three-dimensional or flat structures by means of component jet.

It is known from an article entitled "Buddha by fax" in the periodical *Der Spiegel* 37/1998, pages 259 to 263 to use a program-controlled laser beam to cure liquid synthetic resin to form physical structures. This process is in particular used for model making. According to a further development (page 263), an original shape is recorded by means of a laser scanner. A computer converts this scan into a three-dimensional model and transmits the data via the telephone network or the Internet to a 3-D printer at a different location which produces the model from synthetic resin. This is performed using a 3-D printer (page 263) which is similar to an inkjet printer but instead sprays a liquid binder onto ceramic, steel or starch powder, said binder binding and hardening the powder where it is sprayed.

Ultra-small quantities of the necessary binder are here conveyed and dispensed using micropumps which, for example, operate piezoelectrically with membranes (*LaborPraxis*, November 1997, pages 68 to 76).

The above-stated systems require either a laser beam, which cures a plastic from a liquid composition, or a jet of liquid binder which binds and hardens a loose powder mixture. In both cases, a liquid or pulverulent substance is needed from which a physical structure is built up by the action of the laser beam or the binder.

The disadvantage of the above-stated processes is that the article to be produced must always be fashioned from an existing liquid or pulverulent composition by exposure to a high-energy beam or a jet of binder. The already produced portion of the article must here constantly be kept submerged in unhardened starting material. The resultant article is thus not visible. Once the article is complete, the excess composition must be removed. Even if recycling is possible, this entails considerable costs.

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The object arises of producing three-dimensional or flat structures with the assistance of component jets, wherein this structure always remains free of excess material during production and, in principle, is visible while it is being built up.

5 This object is achieved according to the invention by at least two component jets in the form of small droplets with an average diameter of $<1000\text{ }\mu\text{m}$ consisting of a) at least one polyisocyanate component and b) at least one component capable of forming polymers by reaction with this polyisocyanate component being reacted by being combined.

10 In this manner it is ensured that, when producing three-dimensional or flat structures, such as articles, films or layers, the entirety of the required material is only applied onto a supporting substrate by the two component jets and is optionally further built up thereon by means of the preferably automatically controlled pair of component
15 jets. During production, the support and the structure being built up thereon are, in principle, constantly visible. Excess material is not present during and after production. No such excess thus need be removed nor optionally prepared for recycling.

20 The novel process is suitable for numerous different applications, *inter alia* in particular for the production of structural articles or for firmly applying structures onto a substrate. It is, for example, possible in this manner to produce housing parts, gearwheels, in particular models, three-dimensional faxes, films or layers. In particular, it is possible to apply structures of very fine dimensions, for example in the
25 micro range, onto substrates or other articles, such as for example onto printing films; in particular, it is possible to produce printed products in Braille.

Naturally, a controlled micropump must be present for each component jet to produce the droplets and the component jet. The devices for the component jets must be
30 adjustable and immobilisable relative to each other. This applies in particular to the angle at which the component jets combine and is generally determined empirically, in particular taking account of the viscosity of the components. The angle enclosed by the component jets is usually between 15° and 75° , but may also be greater or lesser

than these values. If the two component jets possess a differing energy, these component jets are adjusted relative to each other such that when the two component jets collide their deflections are of equal magnitude. In this manner, they then have a differing share of the total angle. In order to build up a three-dimensional structural article, the component jets must be appropriately controlled, preferably program-
5 controlled, with regard to the particular position of their active reaction point.

It is particularly advantageous if the component jets combine droplet-by-droplet in order to react.
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The reaction proceeds effectively *per se* merely by the combination of the component jets. However, the greater is the accuracy with which the components are combined precisely drop-by-drop, the better is the reaction product. This is achieved by tuning the frequencies of the component jets one to the other, in particular substantially by
15 taking account of the viscosities of the components, droplet size and the path length from the nozzle outlets to the point of combination, such that at the desired point of collision of the component jets in each case two droplets of a mutually adjusted volume combine in order to react. If the droplets do not collide exactly with each other, mixing in order to react only proceeds by swirling or in the continuing
20 combined jet, wherein greater or lesser deviations from the optimum reaction product may arise.

The component jets are suitably produced, for example, by using dispensing heads or micropumps and controllers from the company microdrop, Gesellschaft für
25 Mikrodosiersysteme mbH, Mühlenweg 21, D-22844 Norderstedt, as are described in the company brochures "MicroDrop-Mikrodosiersysteme", print reference 02-3/98-d, and "Autodrop-Ansteuerungselektronik", print reference 05-3-/98-d. Such devices use a modified inkjet printing process technique comprising a glass capillary with an outlet nozzle enclosed in a piezo actuator. Periodic application of voltage to the piezo
30 actuator produces pressure waves by means of which droplets are expelled at high velocity from the outlet nozzle, with droplets of a volume between 30 and 500 picolitres with a scatter of <1% in particular being dispensed. Up to 2000 droplets per seconds are here expelled. Devices suitable for greater throughputs are those in which

a jet of liquid produced by pressure is modulated with a piezo actuator, as a result of which the jet breaks down into small droplets synchronously with the modulation. In this case, the droplet volume is approx. 100 picolitres to 100 nanolitres at a drop diameter of 60 to 600 μm and a drop frequency of 1000 to 100000 per second.

5 Conventional applications are in microencapsulation, spray drying, powder production or microsphere production, for supplying coolant or lubricant to drill bits, application of biochemical substances, lubrication of watch or clock movement bearings, dispensing of flux for high precision soldered joints in electronics.

10 Naturally, such apparatuses designed for the production of individual jets must be modified in order to produce two colliding component jets, which are intended preferably to combine droplet-by-droplet and thus react.

15 Depending upon the requirements of the structural article to be produced, at least one additive is preferably added in the form of an additional jet.

Alternatively, at least one additive is added to at least one of the components of the component jets a) and/or b).

20 Such an additive for example consists of dye, filler, flame retardant or a foam stabiliser, as is explained in greater detail below.

A structural article is preferably built up on a support element.

25 This method is particularly advantageous for the production of models.

According to one variant, the component jets are combined above the support element.

30 Alternatively, combination proceeds on the support element.

The process variant which is selected is substantially dependent upon the nature of the final product which is to be produced.

The first variant would seem to be more suitable for the production of a structural article, while the second variant may be preferred for the application of structures onto a support element of some kind.

Once the first layer has been produced directly on the support element, a structural article which is to be built up is produced by reaction by combining the components of the component jet thereon or just above it in accordance with the programmed motion of the component jets.

The following starting components are used in the process according to the invention:

The polyisocyanate components used are known polyisocyanates, as are for example described by W. Siefken in *Justus Liebigs Annalen der Chemie*, 562, pages 75 to 136.

The polyisocyanates used according to the invention have at least two isocyanate groups, preferably two to four isocyanate groups, per molecule. Industrially readily available polyisocyanates, such as 2,4- or 2,6-tolylene diisocyanate (TDI), and any desired mixtures of these isomers, are preferably used here. Polyphenylpolymethylene polyisocyanates, as are produced by aniline/formaldehyde condensation and subsequent phosgenation (MDI), may also be considered. 4,4'- or 2,4'-diphenylmethane diisocyanate or mixtures or homologues thereof may be mentioned by way of example. The polyisocyanates to be used according to the invention may be modified by carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups (modified polyisocyanates).

If light-fast products are to be produced, polyisocyanates having isocyanate groups attached to aliphatic hydrocarbon groups are preferably used, such as for example 1,6-diisocyanatohexane, isophorone diisocyanate or 4,4'-dicyclohexylmethane diisocyanate.

Low viscosity polyisocyanates liquid at room temperature are particularly preferably used, such as for example 2,4- and 2,6-diisocyanatotoluene or mixtures thereof or mixtures of 2,4'- and 4,4'-diisocyanatodiphenylmethane.

- The compounds capable of reacting with polyisocyanates which are used are compounds having hydroxyl groups, amine groups, carboxyl groups and/or thiol groups. Preferably, compounds having amine groups and optionally hydroxyl groups are used, optionally also compounds having only hydroxyl groups. Products having a suitable reaction profile and range of properties may purposely be produced by using relatively high molecular weight compounds in combination with low molecular weight compounds and by selecting functionality.
- 10 Relatively high molecular weight organic compounds having at least two hydroxyl groups per molecule and a molar mass of 400 to 12000, preferably of 600 to 10000, particularly preferably of 1000 to 6000, which may be considered are polyesters, polycarbonates, polylactones, polyesteramides, polyethers and polythioethers comprising hydroxyl groups, as are known for the production of polyurethane
- 15 elastomers. The relatively high molecular weight organic compounds preferably have two to three, in particular two hydroxyl groups per molecule. The polyesters comprising hydroxyl groups which may be considered are, for example, reaction products of polyhydric alcohols with polybasic carboxylic acids. The free carboxylic acid may also be replaced by the corresponding carboxylic anhydrides or the
- 20 corresponding carboxylic acid esters of lower alcohols or mixtures thereof. The carboxylic acids may be of an aliphatic, cycloaliphatic, aromatic and/or heterocyclic nature. They may be substituted, for example by halogen atoms, and may optionally also be of an unsaturated nature.
- 25 Examples of such polycarboxylic acids and the derivatives thereof which may be mentioned are: adipic acid, sebacic acid, phthalic acid, phthalic anhydride, tetrahydro- or hexahydrophthalic anhydride, isophthalic acid, trimellitic acid, maleic anhydride, di- and trimerised unsaturated fatty acids, terephthalic acid dimethyl ester and terephthalic acid bis-glycol ester. Polyesters based on adipic acid are preferred.
- 30 Examples of polyhydric alcohols which may be reacted with the carboxylic acids to yield the relatively high molecular weight organic compounds comprising hydroxyl groups and may be considered are: ethylene glycol, 1,2- or 1,3-propanediol, 1,4- or 2,3- or 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,4-bis-

hydroxymethylcyclohexane, 2-methyl-1,3-propanediol, hydroquinone bis(2-hydroxyethyl) ether, resorcinol bis(2-hydroxyethyl) ether, trimethylolpropane, 1,2,6-hexanetriol, pentaerythritol, quinitol, mannitol, sorbitol, formitol, methyl glycoside, together with di-, tri-, tetra- and higher polyethylene, polypropylene and polybutylene glycols.

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Polyethers comprising hydroxyl groups which may be considered are any known polyethers, for example those which are obtained by addition polymerisation of tetrahydrofuran and/or of epoxides, such as ethylene oxide, propylene oxide, butylene oxide, styrene oxide or epichlorohydrin with themselves or by addition of these epoxides, preferably of ethylene oxide and propylene oxide, optionally as a mixture or in succession, onto starter components having reactive hydrogen atoms, such as water, alcohols, ammonia or amines, for example ethylene glycol, propylene glycol, diethylene glycol, dimethylolpropane, glycerol, sorbitol, sucrose, formitol or formose and 4,4'-dihydroxydiphenylpropane, aniline, ethylenediamine or ethanolamine.

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It is optionally possible according to the invention also to use such polyhydroxyl compounds containing high molecular weight polyaddition products or polycondensation products or addition polymerisation products in finely dispersed or dissolved form. Such polyhydroxyl compounds are, for example, obtained by permitting polyaddition reactions (for example reactions of polyisocyanates with amino-functional compounds, such as hydrazine or diamine) or polycondensation reactions (for example between formaldehyde and phenols and/or amines) to proceed *in situ* in the stated compounds comprising hydroxyl groups.

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Polyhydroxyl compounds modified by vinyl addition polymerisation products, which are obtained by addition polymerisation of styrene and/or acrylonitrile in the presence of polyethers or polycarbonate polyols, are also suitable for the process according to the invention. Representatives of the stated relatively high molecular weight polyhydroxyl compounds to be used are listed, for example, in *High Polymers*, vol. XVI, *Polyurethanes, Chemistry and Technology*, edited by Saunders-Frisch, Interscience Publishers, New York, London, volume I, 1962, pages 32 to 42 and pages 44 to 54 and volume II, 1964, pages 5 to 6 and 198 to 199, and likewise in *Kunststoff-Handbuch*, volume VII, 1964, Vieweg & Höchtlen, Carl Hanser Verlag,

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Munich 1966, for example on pages 45 to 71, and in particular in DE-OS 2 920 501, pages 17 to 24. Naturally, mixtures, for example of polyethers and polyesters, may also be used.

- 5 The following compounds may, for example, be considered as low molecular weight organic compounds with at least two hydroxyl groups per molecule and with a molar mass of 62 to 399 (component c): diols, such as ethylene glycol, 1,2- and/or 1,3-propanediol, 1,4- and 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, 1,4-bis-hydroxymethylcyclohexane, 2-methyl-1,3-propanediol, 10 dibromobutanediol, di-, tri-, tetra- and higher polyethylene glycols with a molar mass of up to 399, di-, tri-, tetra- and higher polypropylene glycols with a molar mass of up to 399, di-, tri-, tetra- and higher polybutylene glycols with a molar mass of up to 399, 4,4'-dihydroxydicyclohexylpropane, dihydroxyethylhydroquinone, N-methyldiethanolamine, triols and polyols, such as glycerol, trimethylolpropane, trimethylethane, 15 1,2,4-butanetriol, 1,3,6-hexanetriol, pentaerythritol, quinitol, mannitol, sorbitol, methyl glycoside, compounds of the 1,4-3,6-dianhydrohexitol series, castor oil.

- Further low molecular weight polyhydroxy compounds suitable according to the invention which may be mentioned are ester diols, such as ϵ -hydroxybutyl- ϵ -hydroxy- 20 caproic acid ester, ω -hydroxyhexyl- γ -hydroxybutyric acid ester, together with low molecular weight esters bearing OH terminal groups prepared from polycarboxylic acids and polyalcohols, as are also used for the production of the relatively high molecular weight polyol components, such as for example adipic acid bis-(β -hydroxyethyl) ester and terephthalic acid 1,6-bis-(β -hydroxyethyl) ester; diol urethanes, such 25 as hexamethylene bis-(β -hydroxyethylurethane) or 4,4'-diphenylmethane bis-(ω -hydroxybutylurethane), as well as diol ureas, such as 4,4'-diphenylmethane bis-(β -hydroxyethylurea).

- Further low molecular weight polyols which may be considered are mixtures of 30 hydroxyaldehydes and hydroxyketones ("formose") or the polyhydric alcohols ("formitol") obtained therefrom by reduction, as are obtained on self-condensation of formaldehyde in the presence of metal compounds as catalyst and of compounds

capable of enol formation as co-catalyst (DE-OS 2 639 084, DE-OS 2 714 084, DE-OS 2 714 104, DE-OS 2 721 186, DE-OS 2 738 154 and DE-OS 2 738 512).

Aliphatic polyether-polyamines, as may for example be obtained by reductive amination of polyoxyalkylene glycols with ammonia according to patent specifications BE 634 741 or US 3 654 370, may be used as relatively high molecular weight aliphatic di- and polyamines. Further polyether-polyamines may be produced using methods as are listed in the Texaco Chemical Co. brochure *Jeffamine, Polyoxypropylene Amines*, 1978, for example by hydrogenation of cyanoethylated polyoxypropylene glycols (DE-OS 1 193 671), by amination of polypropylene glycol sulfonic acid esters (patent specification US 3 236 895), by treating a polyoxyalkylene glycol with epichlorohydrin and a primary amine (patent specification FR 1 466 708) or by reacting NCO prepolymers with enamines, aldimines or ketimines comprising hydroxyl groups and subsequent hydrolysis according to DE-A 2 546 536.

Suitable relatively high molecular weight aliphatic di- and polyamines also include the polyamines obtainable according to DE-OS 2 948 419 and DE-OS 3 039 600 via the carbamate stage by alkaline hydrolysis of NCO prepolymers (based on aliphatic diisocyanates) with bases. These relatively high molecular weight polyether-polyamines have molecular weights of approx. 400 to 6000, preferably of 400 to 3000, particularly preferably of 1000 to 3000.

Preferably used relatively high molecular weight amines having amine groups attached to aromatic residues are those which are produced by hydrolysis of compounds comprising aromatically attached, terminal isocyanate groups with an NCO content of 0.5 to 40 wt.%. These compounds containing NCO groups are produced, for example, from polyethers with n terminal hydroxyl groups per molecule and n moles of a diisocyanate, for example 2,4-diisocyanatotoluene. Such hydrolysis processes are presented, for example, in DE-A 3 710 427, DE-A 2 948 419 and EP 97 299.

The following low molecular weight polyamines are used: aliphatic polyamines, such as for example ethylenediamine, 1,2- or 1,3-diaminopropane, 1,4-diaminobutane, 1,6-

5 diaminohexane, isophoronediamine, 4,4'-dicyclohexylmethanediamine and similar aromatic polyamines, such as for example p-phenylenediamine, 2,4-/2,6-tolylenediamines, diphenylmethane-4,4'- and/or -2,4'- and/or -2,2'-diamines, 3,3'-dichloro-4,4'-diaminodiphenylmethane, 3-(C₁-C₈)-alkyl-4,4'-diaminodiphenylmethanes, 3,3'-di-
10 (C₁-C₄)-4,4'-diaminodiphenylmethanes and 3,3', 5,5'-tetra-(C₁-C₄)-alkyl-4,4'-diphenylmethanes, 4,4'-diaminodiphenyl sulfides, sulfoxides or sulfones, 2,4-diaminobenzoic acid esters according to DE-A 2 025 900 as well as tolylenediamines substituted by one or two (C₁-C₄)-alkyl groups. Particularly preferred compounds are 3,5-diethyl-2,4- and/or -2,6-diaminotoluene (in particular the technical (80/20) or
15 (65/35) isomer mixtures thereof), asymmetrically tetraalkyl-substituted diaminodiphenylmethanes, for example 3,5-diethyl-3',5'-diisopropyl-4,4'-diaminodiphenylmethane and the isomer mixtures thereof according to DE-A 2 902 090, 4,4'-diaminobenzanilide, as well as 3,5-diaminobenzoic acid (C₁-C₄)-alkyl esters, 4,4'- and/or 2,4'-diaminodiphenylmethane, 4,4',4''-triaminotriphenylmethane and 1,5-naphthylene-diamine.

The following additives may be used: non-reactive plasticisers, catalysts and further auxiliary substances and additives. Optionally used plasticisers which may be considered comprise not only the *per se* known esters of phthalic acid, trimellitic acid,
20 adipic acid, sebacic acid, azelaic acid, phosphoric acid or sulfonic acids, but also, for example, the esters of oleic acid and stearic acid with compounds containing aliphatically or aromatically attached OH groups, such as for example alcohols or phenols. Examples of such esters are: bis-(2-ethylhexyl) phthalate, benzylbutyl phthalate, tris-(2-ethylhexyl) trimellitate, bis-(2-ethylhexyl) adipate, tricresyl
25 phosphate, diphenylcresyl phosphate, diphenyloctyl phosphate, tris-(2-ethylhexyl) phosphate, (C₁₀-C₁₈)-alkylsulfonic acid phenyl esters. Hydrocarbons, such as so-called butadiene oils or for example diisopropylnaphthalene, may also be used.

Optionally used polyurethane catalysts which may be used are *per se* known
30 polyurethane catalysts, organic metal compounds being particularly effective, optionally together with further, conventional polyurethane catalysts, in particular catalysts containing tert.-amine.

Organic metal compounds which may in particular be considered as catalysts are organic tin, zinc, lead, mercury, iron and bismuth compounds. Organic tin compounds which are preferably considered are tin(II) salts of carboxylic acids, such as tin(II) bis-ethylhexanoate and tin(II) stearate and the dialkyltin salts of carboxylic acids, such as for example dibutyltin dilaurate and dioctyltin diacetate or dialkyltin ester mercaptides. Organic zinc compounds which are preferably considered are zinc bis-ethylhexanoate and zinc bis-acetylacetonate. Organic lead compounds which are preferably considered are not only lead(II) salts of carboxylic acids such as lead(II) naphthenate, lead(II) bis-ethylhexanoate, lead(II) stearate, but also for example lead(II) bis-diethyldithiocarbamate. Phenylmercuric propionate may, for example, be considered as an organic mercury compound. Iron(III) acetylacetonate may, for example, be considered as an organic iron compound, while bismuth(III) ethylhexanoate and bismuth(III) neodecanoate may be considered as organic bismuth compounds. Compounds containing lead and mercury are, however, less preferred for reasons of environmental protection and occupational hygiene.

The following may be mentioned as examples of catalysts containing tert.-amine: triethylamine, tributylamine, N,N,N',N'-tetramethylethylenediamine, 1,4-diazabicyclo[2.2.2]octane, N,N-dimethylbenzylamine, N,N-dimethylcyclohexylamine.

Further representatives of catalysts to be used according to the invention and details of the mode of action of the catalysts are described in *Kunststoff-Handbuch*, volume VII, edited by Vieweg & Höchtlen, Carl Hanser Verlag, Munich, 1966, for example on pages 96 to 102. The catalysts are generally used in a quantity of between approx. 0.001 and 10 wt.%, relative to the complete composition.

The following may be mentioned as examples of further optionally used auxiliary substances and additives: dyes, pigments, fillers such as silica gel, gypsum, talcum, calcium carbonate, barium sulfate, carbon black, activated carbon, metal powder, UV absorbers or stabilisers, such as phenolic antioxidants, light stabilisers, surface-active additives such as surfactants or levelling auxiliaries, antiblocking agents, silicones, flame retardants or fungistatically and/or bacteriostatically active substances. Further

auxiliary substances and additives known *per se* from coatings technology, such as rheological auxiliaries or solvents, may also be present.

General setup of a test apparatus:

- 5 The test apparatus consists of two MD-K-140 H piezoelectrically operating dispensing heads (brochure 02-3/98-d from the above-mentioned company microdrop) with a nozzle diameter of 100 μm and two AD-E-110 dispensing head drivers and an AD-E-130 pressure supply (both according to brochure 05-3/98-d from the above-mentioned company microdrop). Component a) is polyisocyanate, while
- 10 component b) is a mixture prepared from 86.5 wt.% of a polyether with NH_2 terminal groups synthesised from propylene oxide units and a molecular weight of 400 (Jeffamin D400 = trade name of the company Texaco Chemical Deutschland GmbH, D-20459 Hamburg) and 13.5 wt.% of diethyltolylenediamine distillate (Ethacure 100 = trade name of the company Albemarle Corp., B 1050 Brussels, Belgium), which are
- 15 dispensed in a 1:1 ratio by weight with a droplet diameter of 60 to 70 μm at a frequency of 500 Hz. The dispensing heads are adjusted relative to each other such that, after 3.2 mm, the droplet jets they produce combine with reaction to form a common droplet jet.

Example 1:

5 The polyisocyanate used is a polyisocyanate mixture of the diphenylmethane series with an isocyanate group content of 31 wt.%, a dicyclic fraction of 55 wt.% and a viscosity of 130 mPa*s at 25°C. The dispensing heads are guided over the surface of a conventional commercial microscope slide in such a manner that the individual droplets of the two component jets collide exactly on the surface of the support. At an atmospheric humidity of below 10% relative humidity, a 20*20 dot matrix of polyurethaneurea dots, each dot comprising one drop of polyisocyanate and one drop
10 of amine mixture, with a dot spacing of 500*500 µm, is produced on the slide.

Example 2:

15 A matrix of polyurethane dots, each dot comprising 10 drops of polyisocyanate and 10 drops of amine mixture, was produced in a similar manner to Example 1.

Example 3:

20 A continuous line of polyurethane 20 mm in length is produced in a similar manner to Example 1 by setting down dots side by side, each dot comprising one drop of polyisocyanate and one drop of amine mixture.

Example 4:

25 A continuous line of polyurethane 20 mm in length is produced in a similar manner to Example 3. The polyisocyanate used is an isocyanate mixture comprising 40 wt.% 2,4'-diphenylmethane diisocyanate and 60 wt.% 4,4'-diphenylmethane diisocyanate.

Example 5:

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Using the isocyanate mixture according to Example 4 and the method described in the general test setup, polyurethane structures approx. 20 mm in height with diameters of

between 0.5 and 1 mm are built up on a microscope slide without using moulds or supporting means.

Patent Claims

1. Process for the production of three-dimensional or flat structures by means of component jet, characterised in that at least two component jets in the form of small droplets with an average diameter of $<1000\text{ }\mu\text{m}$ consisting of a) at least one polyisocyanate component and b) at least one component capable of forming polymers by reaction with this polyisocyanate component are reacted by being combined.
2. Process according to claim 1, characterised in that the component jets are combined droplet-by-droplet.
3. Process according to claim 1 or 2, characterised in that at least one additive is added in the form of at least one further jet.
4. Process according to claim 1 or 2, characterised in that at least one additive is added to at least one of the components of the component jets a) and/or b).
5. Process according to one of claims 1 to 4, characterised in that a three-dimensional article is built up on a support element on reaction of the colliding jets.
6. Process according to claim 5, characterised in that the jets of the components are combined above the support element.
7. Process according to claim 5, characterised in that the jets of the components are combined on the support element.
8. Process according to one of claims 1 to 6, characterised in that polyamines alone or in combination with others as the sole or partial component are used as the component for jet b).

9. Process according to one of claims 1 to 8, characterised in that the component jets are sprayed in an atmosphere with a relative atmospheric humidity of <40%.

Process for the production of three-dimensional or flat structures**A b s t r a c t**

- 5 Three-dimensional or flat structures may be produced without excess material while remaining visible during the process by reacting at least two component jets in the form of small droplets with an average diameter of $<1000 \mu\text{m}$ consisting of a) at least one polyisocyanate component and b) at least one component capable of forming polymers by reaction with this polyisocyanate component, by combining them.
- 10

10/049403-10

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

METHOD FOR THE PRODUCTION OF THREE-DIMENSIONAL OR FLAT STRUCTURES

the specification of which is attached hereto,

or was filed on July 28, 2000

as a PCT Application Serial No. PCT/EP00/07280

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 37 770.7
(Number)

Germany
(Country)

August 10, 1999
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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